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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C10G 32/00, 27/12, 27/14, C10L 9/06	A1	(11) International Publication Number: WO 00/15734 (43) International Publication Date: 23 March 2000 (23.03.00)
(21) International Application Number: PCT/US99/21478 (22) International Filing Date: 16 September 1999 (16.09.99) (30) Priority Data: 60/100,576 16 September 1998 (16.09.98) US (71)(72) Applicant and Inventor: JEANBLANC, James, K. [US/US]; 400 NW Ninth Street, Galva, IL 61434 (US). (74) Agents: WHEELER, George, F. et al.; McAndrews, Held & Malloy, Ltd., Suite 3400, 500 W Madison Street, Chicago, IL 60661 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DESULFURIZATION PROCESS (57) Abstract <p>Sulfur-containing carbonaceous materials are desulfurized by reaction with a mixture of an oxidizing agent and an oxygenated solvent such as diethyl ether under alkaline conditions at a temperature preferably ranging from ambient temperature to about 250 °F (121 °C) and a preferred pressure of about 1 atmosphere to 2 atmospheres. The use of radiation – such as X-ray, infrared, visible, microwave, or ultraviolet radiation, alpha, beta, or gamma radiation, other atomic radiation emanating from a radioactive material, or ultrasound – facilitates desulfurization. The products of the reaction are a desulfurized carbonaceous material in which the sulfur content is (for example) less than about 1 % and separated sulfur compounds.</p>		

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The sulfur in carbonaceous materials may be present in various combined forms including heteroaromatic compounds. Such compounds are difficult to desulfurize because desulfurization requires breaking various bonds including the relatively strong carbon-to-sulfur bond, C-S, as well as the weaker sulfur-to-sulfur, S-S, sulfur-to-oxygen, S-O, and sulfur-to-hydrogen, S-H, bonds.

Removal of these combined forms of sulfur has proven difficult. The sulfur compounds are objectionable because combustion of fuels containing them as contaminants results in the release of flue or exhaust gas containing sulfur oxides, which are noxious and corrosive and present a serious problem with respect to pollution of the atmosphere. High-sulfur petroleum products such as diesel fuel, other fuel oils, and gasoline are also subject to sulfur content restrictions, based on their impact on the environment when they are used as fuels.

Various processes have been used in the past to remove objectionable sulfur-containing compounds from coal and petroleum. U.S. Patent No. 4,548,708, issued to Schwarzer, et al. on October 22, 1985, claims: "A process for substantially complete elimination of hydrogen sulfide from the organic phase of natural gas, crude oil or mixtures thereof, consisting essentially of the step of reacting, by mixing, the natural gas, crude oil or mixture thereof, with an aqueous reagent consisting essentially of from about 20 to 50% aqueous hydrogen peroxide, without the addition of any catalysts or organic compounds or of compounds that yield them, at a pressure of at least about 90 kPa gauge and a reaction temperature of up to the decomposition temperature of hydrogen peroxide to remove the hydrogen sulfide from the organic phase." 90 kPa is understood to be about 13 psi, which is slightly less than atmospheric pressure.

U.S. Patent No. 2,744,054, issued to Pieters, describes the conversion of mercaptans to disulfides in a hydrocarbon, by treatment with an aqueous hydroxide, free oxygen, and a peroxide. Pieters does not, however, describe removing sulfur from the hydrocarbon.

See also the following references. U.S. Patent No. 1,950,735, issued to Levine, discusses the use of a metallic chloride to remove sulfur. U.S. Patent No. 3,964,994, issued to Kelly, discloses the use of hydrogen peroxide to sweeten hydrocarbons. U.S. Patent Nos. 4,097,244 and 4,105,416, issued to Burk, Jr. et al., disclose methods for reducing the sulfur content of coal by treating it with an iron complexing agent and an oxidant, then heating the coal or treating it with hydrogen. U.S. Patent No. 4,121,998, issued to Frame, discloses a

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catalytic process for sweetening a sour petroleum distillate. U.S. Patent No. 4,481,107, issued to Urban, discloses oxidizing the mercaptans in a hydrocarbon fraction, using a hydrocarbon-soluble alkali metal compound and a metal chelate catalyst. U.S. Patent No. 5,310,479 discloses reducing the sulfur content of crude oil by treating it with hydrogen peroxide and formic acid, then washing the product. U.S. Patent No. 5,593,932, issued to Gillespie et al., discloses a process for sweetening a sour hydrocarbon fraction using a mixture of a supported metal chelate and a solid base.

In addition, sodium hydroxide or potassium hydroxide solutions have been used to treat petroleum fractions boiling in the general range below about 700°F (370°C). Extraction with a liquid solvent, such as sulfuric acid, sulfur dioxide, or furfural has also been used, as has adsorption on suitable materials, such as activated bauxite, charcoal, or clay. Mercaptans have been converted into disulfides and polysulfides by plumbite treatment or treatment with hypochlorite or copper salts. Many catalytic processes, generally utilizing hydrogen under high pressure and temperature conditions, have also been developed.

The use of high pressures and temperatures to desulfurize various materials has proved successful to some extent in the past. But the high energy input necessary has required the use of specialized and expensive apparatus for this purpose and has made desulfurization expensive.

It would be desirable to provide a process which is effective for removing sufficient sulfur from coal, crude oil, or petroleum fractions contaminated with sulfur-containing compounds to result in a product containing, for example, less than about 1% sulfur. Since petroleum fractions, such as heavy crudes, may contain as much as about 8-12% sulfur, such a process would represent removal of about 85-95% of the sulfur contaminant in such petroleum fractions.

It is accordingly an object of the present invention to provide a process that is effective to remove a substantial proportion of the sulfur that contaminates various carbonaceous materials.

It is another object of the present invention to provide such a process that utilizes readily available reactants.

Another object of this invention is to provide a process that can be operated at moderate temperatures and pressures.

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A further object of the present invention is to provide a process for desulfurizing coal, petroleum products, and other sulfur-contaminated carbonaceous materials, which process is economical to operate and requires a minimum of specialized equipment.

Other objects and advantages of the present invention will become apparent during the course of the following detailed description and disclosure.

BRIEF SUMMARY OF THE INVENTION

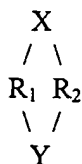
The present invention accomplishes at least one of the above-described objects, in whole or in part, by providing a process for removing sulfur from sulfur-containing compounds present in coal, petroleum, petroleum fractions, and other sulfur-containing carbonaceous materials.

One aspect of the invention is a process for removing sulfur from sulfur-containing carbonaceous materials. In this aspect of the invention a carbonaceous material requiring desulfurization is treated with a source of activated oxygen and with a source of energy, which each reduce the sulfur content of the carbonaceous material.

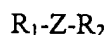
The source of active oxygen used in the treatment step is maintained under basic conditions effective to reduce the sulfur content of the carbonaceous material.

The carbonaceous material is exposed to a source of energy of a type and under conditions effective to further reduce the sulfur content of the carbonaceous material, compared to its sulfur content with the same active oxygen treatment, but without the energy treatment.

Another aspect of the invention is also a process for removing sulfur from sulfur-containing carbonaceous materials. In this aspect of the invention a carbonaceous material requiring desulfurization is treated with a source of activated oxygen and with a solvent having one of the following structures:



and



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wherein X and Z are each $-O-$; Y is independently selected from $-O-$, $-OR_2O-$ or a direct linkage between R_1 and R_2 ; R_1 is selected from hydrogen or an independently selected R_2 as defined below; R_2 is selected from straight or branched chain alkyl, alkenyl, or alkynyl having from 1 to 16 carbon atoms, aralkyl having a single ring or multiple ring aryl having from 6 to 24 carbon atoms attached to a straight or branched chain alkyl, alkenyl, or alkynyl as previously defined; under basic conditions effective to reduce the sulfur content of the carbonaceous material.

Yet another aspect of the present invention is a low-sulfur carbonaceous material, made according to one of the processes described above.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The advantages and features of the present invention will be better understood by the following description when considered in conjunction with the accompanying drawing, in which the Figure is a schematic flow chart of a typical process in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for desulfurizing carbonaceous materials which contain compounds in which sulfur is present. The process provides a means for removing sulfur from coal, petroleum fractions, and other organic materials in which sulfur is present as various sulfur-containing organic compounds.

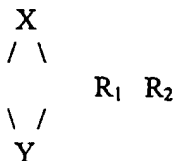
The present invention, rather than utilizing high pressures and temperatures for energy input, requires only low pressures and moderate temperatures and takes advantage of the energy produced by an exotherm that occurs during the process. The exotherm takes place under basic conditions and requires little, if any, adjustment of the temperature and pressure; rather, the reaction proceeds under relatively mild conditions, including ambient or slightly elevated temperatures and a pressure which can range from a vacuum to ambient or higher. In general, temperatures ranging from about 32°F (0°C) to about 250°F (121°C) are used. Temperatures of about 120°F (49°C) to 250°F (121°C) are contemplated. Ambient temperature may also be used. Pressures generally range from close to zero atmospheres absolute pressure (i.e. a partial vacuum) to ambient pressure to 2 atmospheres or more (gauge

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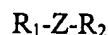
pressure). A pressure below ambient has been found useful, particularly to lower the effective boiling point of the solvent and to facilitate pulling off and removing the solvent and gaseous sulfur compounds.

The carbonaceous materials contemplated for use in the present invention include, but are not limited to, petroleum and its fractions and other products, as identified previously; bituminous coal, anthracite coal, coal precursors such as lignite, and fractions and other products of any of the foregoing. More broadly, any fossil fuel containing sulfur is contemplated to benefit from the present treatment. In addition to fossil fuels, any organic residue containing sulfur is contemplated for use in the present process.

The desulfurizing reaction is preferably carried out in the presence of a solvent. The useful solvents include mutual solvents for hydrocarbons and water, such as ethers, ketones, aldehydes, alcohols, and other relatively polar organic solvents. Suitable solvents have either of the following structures:



or



In these compounds, X and Z are independently selected from C=O (a carbonyl linkage) and -O- (an ether linkage). Optionally, X and Z may be more specifically defined as ether linkages. Y is independently selected from -O-, -OR₂O- or a direct linkage between R₁ and R₂. R₁ is selected from hydrogen or an independently selected R₂ as defined below. R₂ is selected from straight or branched chain alkyl, alkenyl, or alkynyl having from 1 to 16 carbon atoms, aralkyl having a single ring or multiple rings, aryl having from 6 to 24 carbon atoms attached to a straight or branched chain alkyl, alkenyl, or alkynyl as previously defined.

Ethers, broadly defined as any of the above-stated structures including one or more ether linkages, are one type of solvents contemplated for use in the process of the present invention. However, to provide a convenient temperature range for operation of the process, the ether can be a relatively low boiling compound to operate under mild conditions of

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temperature and pressure. Diethyl ether, having a boiling point of 94.1°F (34.5°C), or isopropyl ether, having a boiling point of 153.3°F (67.5°C) are suitable. Other aliphatic or aromatic ethers can also be used with appropriate temperature and pressure adjustments. These include butyl ether, having a boiling point of 108°F (42°C), ethyl methyl ether, having
5 a boiling point of 51.4°F (10.8°C), or ethyl n-butyl ether, having a boiling point of 198°F (92.2°C). Cyclic ethers, such as tetrahydrofuran, having a boiling point of 150.8°F (66°C) or dioxane, having a boiling point of 214.3°F (101.3°C) can also be used. Other contemplated ethers include furan and other furans, α -pyran, γ -pyran, and other pyrans, 1,3,5-trioxane, s-trioxane, ethylene oxide, propylene oxide, other oxiranes, and others.

10 Other suitable solvents are ketones, for example dialkyl ketones such as acetone or methyl isobutyl ketone, aldehydes such as formaldehyde or acetaldehyde, and alcohols such as methanol or ethanol.

A solvent specifically contemplated for the present use is a low-boiling mutual solvent for the carbonaceous material and the oxidizing agent, where one exists. For
15 example, if the oxidizing agent is aqueous hydrogen peroxide and the carbonaceous material is fuel oil, diethyl ether or acetone are suitable solvents. Coal presents a greater solubility problem, due to its substantial free carbon content. However, a solvent for the soluble portions of coal can be used. Again, specific solvents contemplated for coal include any of the foregoing solvents, including acetone and diethyl ether.

20 As the oxidizing agent or source of active oxygen, a peroxide such as hydrogen peroxide or an alkali metal (e.g. sodium) peroxide is contemplated. Organic peroxides such as tertiary butyl hydroperoxide, cyclohexanone peroxide, dicumyl peroxide, and the like can also be used, if desired. Hydrogen peroxide can be used in the form of an aqueous solution containing, for example, from about 10% to 60% hydrogen peroxide. 30% hydrogen peroxide
25 in water is a convenient source of peroxide. Another contemplated oxidizing agent that provides active oxygen is ozone. Ozone is conventionally generated at the point of use, as it is not stable. Ordinary ozone-generating equipment can be used. Free oxygen in gaseous or dissolved form may also be utilized as part or all of the oxygen. A water-soluble source of active oxygen is suitable. Oil-soluble peroxides, particularly organic peroxides, can also be
30 used.

For achieving basic conditions for the exothermic reaction to occur, a base, for example a water-soluble base, more particularly a water-soluble hydroxide, is generally

utilized. Sodium hydroxide or potassium hydroxide are contemplated for this purpose. Other hydroxides that can be used include ammonium hydroxide and calcium hydroxide. Basic materials that are not hydroxides, such as sodium carbonate, can also be used if desired.

The preferred order of mixing of reactants is to add the solvent to the coal or petroleum fraction, followed by adding a mixture of the base and the oxidizing agent. An exothermic reaction ensues and the volume of the reaction mixture expands to, as a non-limiting example, 3 to 15 times its original volume, while the temperature increases. When the process is conducted at ambient conditions, the temperature increases to from about 130°F (54°C) to about 150°F (66°C). During the reaction, a substantial amount of gaseous products is formed, which may be recovered. Following completion of the reaction, any water present can be removed by distillation or by any other oil/water separation process.

Alternatively, the process can be conducted as a continuous process in which the reactants are introduced continuously and, if desired, heat is added to a reaction vessel. Temperatures in the range of about 120°F (49°C) to 250°F (121°C) are generally maintained in the reaction vessel during operation of such continuous process.

In a preferred embodiment of the invention the removal of sulfur is enhanced by the use of radiation, such as alpha radiation, beta radiation, gamma radiation, x-radiation, other radiation that is the product of radioactive decay, ultraviolet radiation, visible light radiation, infrared radiation, microwave radiation, ultrasonic energy, and combinations thereof. Any type and intensity and manner of application of radiation or other energy input that is effective to increase the removal of sulfur from the carbonaceous material can be used.

The inventor contemplates that the effect of the radiation is to excite the molecules involved in the reaction and facilitate bond breaking to release sulfur and/or facilitate the formation of sulfur gases, once the sulfur is freed. Its primary effect may be to promote the reaction of sulfur and activated oxygen atoms to form S-O bonds before the activated oxygen atoms combine with each other to form O₂ molecules. This theory is regarded as a possible explanation of the effect of the radiation, however, and not as a requirement of the invention or any limitation on its scope.

For example, x-rays can be provided having the wavelength and intensity of x-rays used in analytical equipment to cause the molecule or atom being analyzed to fluoresce. Other types, wavelengths, and intensities of radiation can be used as well. The radiation

parameters can be readily determined by a skilled person who is aware of the present invention.

The principal products of the reaction are a carbonaceous material, such as coal, crude oil, refined oil, or a hydrocarbon fraction, containing less than about 1% sulfur and a mixture
5 of gaseous products and salts including predominantly hydrogen sulfide, but also containing some sulfur dioxide, as well as other compounds of sulfur. The gaseous and aqueous products can easily be separated from the carbonaceous material.

If desired, the hydrogen sulfide can be utilized in a Claus process for conversion of the hydrogen sulfide content of the gaseous product to elemental sulfur. Sulfur oxides can be
10 recovered from the water recovered after consumption of the hydrogen peroxide, as by the conventional process of adding lime to precipitate calcium sulfate. Calcium sulfate is gypsum, and can be used to make wallboard, plaster of Paris, and other useful products. Sulfur oxides can also be used to make sulfuric acid. The hydrogen sulfide produced can also be converted to sulfur oxides by reaction with oxygen (as by burning it), then further treated
15 as previously described.

The treatment can be carried out on carbonaceous materials initially containing various amounts of sulfur, and can be carried out to different degrees, resulting in various amounts of residual sulfur in the treated carbonaceous material. As one example, the carbonaceous material feed can be classified as a high-sulfur fuel, and the treated
20 carbonaceous material can be classified as a low-sulfur fuel, under the United States Environmental Protection Agency (EPA) standards, generally effective (except where deviations are permitted) as of January, 2000, reducing by half the amount of sulfur that can be in fuels. Alternatively, the low-sulfur fuel can be fuel complying with current European standards requiring fuel to contain no more than about 0.05% elemental sulfur.

25 The degree of treatment can also be expressed in terms of initial sulfur versus residual sulfur. For example, the carbonaceous material as provided can contain at least about 2% by weight sulfur (expressed as percent by weight elemental sulfur unless otherwise indicated herein); alternatively at least about 3% sulfur; alternatively at least about 4% sulfur; alternatively at least about 5% sulfur; alternatively at least about 6% sulfur; alternatively at
30 least about 7% sulfur; alternatively at least about 8% sulfur; alternatively at least about 9% sulfur; alternatively at least about 10% sulfur; alternatively at least about 11% sulfur; alternatively at least about 12% sulfur.

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The carbonaceous material after the contacting step can contain less than about 1% by weight sulfur; alternatively less than about 0.9% by weight sulfur; alternatively less than about 0.8% by weight sulfur; alternatively less than about 0.7% by weight sulfur; alternatively less than about 0.6% by weight sulfur; alternatively less than about 0.5% by weight sulfur; alternatively less than about 0.4% by weight sulfur; alternatively less than about 0.3% by weight sulfur; alternatively less than about 0.2% by weight sulfur; alternatively less than about 0.1% by weight sulfur, alternatively no more than about 0.05% sulfur, alternatively less than about 0.05% sulfur, alternatively less than about 0.04% sulfur, alternatively less than about 0.03% sulfur, alternatively less than about 0.02% sulfur, alternatively less than about 0.01% sulfur, alternatively less than about 0.005% sulfur. An ordinarily skilled person can readily determine how much to reduce the sulfur content, or how much it can be reduced, within the scope of the present invention. This can be done by optimizing process conditions.

In the following description of the process the carbonaceous material to be desulfurized will be exemplified as a petroleum fraction or basic crude oil. It is to be understood, however, that the process is similarly applicable to coal or coal slurries as well as to other solid and liquid carbonaceous materials. The necessary modifications to the process to process coal slurries will be obvious to a skilled person. For example, water does not need to be separated from the coal slurry before it can be conveyed to a burner that employs an aqueous coal slurry directly as fuel.

Turning now to the drawing, a tank identified by the reference character 10 is used for storing a petroleum fraction or crude oil (or alternatively another carbonaceous material, preferably a fluidized material such as a slurry of coal in water or air-conveyed coal powder). This carbonaceous material is introduced into a mixing vessel 16 through a conduit 12 and a pump 14. Diethyl ether or another solvent is introduced into the mixing vessel 16 from a storage tank 18 through a conduit 20 and a pump 22. A mixture of the carbonaceous material and solvent from the mixing vessel 16 is introduced into a pump mixer vessel 30 through the conduits 24 and 26 and a pump 28. Sodium hydroxide or another base from a storage tank 32, either in solid form or as a concentrated aqueous solution, is introduced into a motionless mixer 40 through the conduits 34 and 36 and a pump 38. Hydrogen peroxide or another oxidizing agent, optionally dissolved in water, is introduced from a storage tank 42 into the motionless mixer 40 through the conduits 34 and 44 and a pump 46.

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A mixture of the base and the oxidizing agent from the motionless mixer 40 is mixed with the mixture of the carbonaceous material and the solvent from the mixing vessel 16 through a conduit 48. The mixture is introduced into the pump mixer 30 through a conduit 24. The mixture of the carbonaceous material, the solvent, sodium hydroxide the base, and the oxidizing agent is introduced into a reactor-separator 52 through a conduit 50.

Following the reaction, the gases and low boiling point organic fractions, including light oils, are vaporized and exit the reactor-separator 52. These gases and low-boiling fractions are introduced into a reflux condenser 56 through a conduit 54. The non-condensable sulfur gases are introduced into a knock-out pot 60 through a conduit 58 and flow to a Claus plant, sulfuric acid production plant, and/or lime process plant through a conduit 62. The condensate is removed through a conduit 64, recycled to the reactor-separator 52 through a conduit 66, and recycled to the mixing vessel 16 through a conduit 68. The light oil product is removed from the reactor-separator 52 through a conduit 70, cooled in a light oil product cooler 72, and passed to storage through a conduit 74.

The resulting water and desulfurized higher boiling point oils descend to the bottom of the reactor-separator 52, where they are removed through a conduit 76 and introduced into a crude product cooler 78. The cooled product is removed from crude product cooler 78 through a conduit 80 and separated from water and salt in an oil-water separator 82. The desulfurized crude product is removed from the oil-water separator 82 through a conduit 84 and passed to storage. Water and salt are removed from the oil-water separator 82 through a conduit 86 and passed to wastewater treatment. A steam heated reboiler 88 reheats a portion of the product stream from the bottom of the reactor-separator 52 taken off through the conduits 90 and 92.

The principal products of the exothermic reaction are desulfurized carbonaceous materials containing less than about 1% sulfur, sulfur-containing gases, and sulfur-containing salts, for example, hydrogen sulfide, sulfur dioxide, and carbonyl sulfide.

If radiation is to be introduced to further eliminate sulfur, it can be provided at various points in the production process. For example, referring to the Figure, the pump-mixer 30 can be provided with a source 90 of x-rays so the reaction mixture is irradiated as the components are initially mixed together. The inventor contemplates that the reaction mixture can also be irradiated by suitable equipment associated with the conduit 50 or the reactor-separator 52, or in a separate vessel adapted for that purpose.

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The inventor contemplates that the radiation can be introduced while the reaction is still occurring after adding the mixture of a base and an oxidizing agent to the solvent-laden coal or petroleum fraction. The inventor has a theory that this manner of providing the radiation will facilitate formation and release of sulfur gases by enhancing the contact of the freed sulfur with the oxygen atoms before the sulfur can have a secondary reaction to reattach to the hydrocarbon or other carbonaceous material, and before the freed oxygen atom stabilizes to form O₂ molecules. This theory is regarded as a possible explanation of the effect of the radiation, however, and not as a requirement of the invention or any limitation on its scope.

Coal can be treated by using the reactants in similar order. Conveniently, the coal may be used in the form of a slurry in water, as it is often supplied to the boilers of electric power plants and other coal-fired combustors. In addition, it is anticipated that the invention can be used in combination with other physical coal cleaning processes including but not limited to coal washing. Because the initial reactant is water soluble, water may be used to lessen the reactant costs in reducing sulfur from coal.

This description of a suitable reaction apparatus and process is merely exemplary of the wide range of apparatus and processes that can readily be devised and used by a person skilled in the art of desulfurizing carbonaceous material.

The invention is exemplified as follows:

EXAMPLE 1

50 mL of heavy California crude oil were mixed with 10 mL of anhydrous diethyl ether in a 600 mL beaker on a stir plate with a stir pellet, which was used throughout the process to stir the contents of the 600 mL beaker. No heat was added, apart from the inherent heat of reaction and dissolution.

15 pellets of sodium hydroxide (4.49 grams) were added to 15 mL of 30% hydrogen peroxide in a 100 mL beaker. This mixture in the 100 mL beaker was swirled by hand until the pellets were completely dissolved.

At the height of its reaction, when it was ready to boil over, the mixture in the 100 mL beaker was added to the mixture in the 600 mL beaker. There was an extreme exotherm in dissolving the sodium hydroxide pellets in the hydrogen peroxide (to the point that the 100 mL beaker could not be held without insulation, had it not been emptied into the 600 mL beaker.)

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The hydroxide and peroxide mixture was added to the crude oil plus diethyl ether mixture. The combined mixture reacted to expand higher than the top of the 600 mL beaker and would have overflowed except for a funnel attached to a vacuum, which was placed on top of the beaker to remove the gases that were formed. Within less than one minute the reaction subsided in size but continued releasing gases with relatively large gas bubbles forming. The reaction continued and at 35 minutes the reaction mixture was poured into two vials. Vial A was capped while vial B was left open.

EXAMPLE 2

A sample was immediately drawn from Vial A and analyzed by x-ray fluorescence using an Oxford Lab X 3000 analyzer. The analysis immediately showed 1.41% sulfur and then showed rapid decreases in the sulfur content in four additional analyses used to create an average reading. The four subsequent measurements each dropped until the fifth showed 0.76% sulfur after less than 8 minutes. A second analysis was immediately run at the completion of the first and it showed further dropping but at a much slower rate, decreasing from 0.68% to 0.66%. The results are shown in Table 1.

TABLE 1

VIAL A - ANALYSIS RESULTS

<u>Treatment Time Elapsed, min.</u>	<u>Sulfur, %</u>
0 (before reaction or radiation)	2.69
35 (reaction and radiation)	1.41
42 " " "	0.66
1089 " " " (~18 hours)	0.72
1403 " " " (~23 hours)	0.67

EXAMPLE 3

Substantial outgassing continued in Vial B, which was left uncovered. It continued to the point of overflowing into a small pan that had been placed under the vial to capture overflow. The next morning, approximately 1/3 of the amount in the vial had overflowed into the pan. A sample was drawn and tested in the Oxford Lab X 3000 analyzer. The results are shown in Table 2.

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TABLE 2**VIAL B - ANALYSIS RESULTS**

<u>Time Elapsed, min.</u>	<u>Sulfur, %</u>
0 (before reaction or radiation)	2.69
1180 (radiation time zero)	2.22
1331	0.87
1354	0.76
1405	0.67

The sulfur content in the initial test (after reacting overnight without the radiation from analysis) was 2.22%, as shown in the preceding table. The sulfur content dropped to 2.13% by the end of five consecutive analyses, resulting in an average of 2.18%. When the sulfur content in the sample was tested again 151 minutes after the first introduction of x-rays (total elapsed time since the start of reaction: 1331 minutes), the sulfur content had dropped to 0.87%. When tested 174 minutes after the first introduction of x-rays (total elapsed time since the start of reaction: 1354 minutes), the sulfur content had dropped to 0.76%. When tested 225 minutes after the first introduction of x-rays (total elapsed time since the start of reaction: 1405 minutes), the sulfur content had dropped to 0.67%.

The crude oil used in Example 1 and Example 2 were both drawn from the same source, and were exposed to the same reactants. Example 2 had only dropped from the untreated California heavy crude sulfur content of 2.69% to 2.22% after 1180 minutes. After exposure to radiation during the analysis it went to 0.76% within an additional 174 minutes.

The inventor has a theory to explain why the sulfur content decreased rapidly when the sample was analyzed. The theory is that the irradiation of the sample with x-radiation in the course of analysis broke sulfur bonds already weakened by the hydroxide-peroxide reaction and mobilized the sulfur atoms and/or the activated oxygen of the peroxide, to induce further reaction between them, or mobilized the transfer of the sulfur-containing reaction products to the aqueous phase of the system. This theory is regarded as a possible explanation of the effect of the radiation, however, and not as a requirement of the invention or any limitation on its scope.

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EXAMPLE 4

50 mL of a slurry of finely divided coal in water are mixed with 10 mL of diethyl ether in a 600 mL beaker on a stir plate with a stir pellet, which is used throughout the process to stir the contents of the 600 mL beaker. No heat is added, apart from the inherent heat of reaction and dissolution.

15 pellets of sodium hydroxide (4.49 grams) are added to 15 mL of 30% hydrogen peroxide in a 100 mL beaker. This mixture in the 100 mL beaker is swirled by hand until the pellets are completely dissolved.

When it is ready to boil over, the mixture in the 100 mL beaker is added to the mixture in the 600 mL beaker. The combined mixture reacts, releasing gases with relatively large gas bubbles forming. The coal slurry is analyzed and found to contain less sulfur after the reaction than before. After sulfurous gases and ether are separated, the coal slurry is found to be suitable for use as fuel in a coal-slurry fueled burner. Alternatively, the process water is separated from the coal slurry by screening to remove residual salts, then additional water is added to provide a fluid slurry suitable for use as fuel.

EXAMPLE 5

The process of Example 1 was essentially repeated, except that the solvent employed was acetone instead of ether, and the ratios of reactants and solvent (all referred to as reactants in Table 3) were changed. The oil sample was heavy California crude having an initial sulfur content of 2.67% by weight in each case. The results are summarized in Table 3.

TABLE 3**Acetone Study**

<u>Run and description</u>	<u>Test sample container open or closed</u>	<u>Time from Experiment to analysis</u>	<u>% sulfur remaining</u>
1a: Nominal reactants	open	2 days	1.76%
1b: same as 1a	closed	2 days	1.52%
2a: increasing reactant 1	--	1 day	0.70%

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2b: same as 2a	--	2 days	0.25%
3a: increasing reactant 2	closed	2 days	1.13%
3b: same as 3a	open	2 days	0.98%
4a: increasing reactant 3	closed	2 days	1.48%
4b: same as 4a	open	2 days	3.85%
5a: decreasing reactant 1	closed	2 days	2.46%
5b: same as 5a	open	2 days	2.28%

As Table 3 illustrates, the acetone solvent allowed the desulfurization to proceed, with the introduction of analytical x-rays, but the reduction of sulfur was much more pronounced
5 when the reaction mixture was analyzed two days after it was formed. This indicates that the reaction proceeded much more slowly in acetone than in ether, requiring slightly less than one day for the sulfur content to reduce below 0.7%, compared to eight minutes using ether. The inventor theorizes that the difference between the two solvents is that the ether solvent provided a less viscous reaction mixture, allowing more mobility for the reactants. This
10 theory is regarded as a possible explanation of the effect of the choice of solvent, however, and not as a requirement of the invention or any limitation on its scope.

The foregoing detailed description is to be clearly understood as given by way of illustration and example only, the spirit and scope of this invention being limited solely by the appended claims.

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CLAIMS

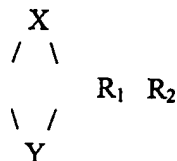
What is claimed is:

- 5 1. A process for removing sulfur from sulfur-containing carbonaceous materials, comprising:
- 10 A. providing a carbonaceous material containing sulfur;
- B. contacting said carbonaceous material with a source of active oxygen in the presence of a base, using amounts of said active oxygen and said base effective to reduce the sulfur content of said carbonaceous material; and
- 15 C. exposing said carbonaceous material to a source of energy of a type and under conditions effective to further reduce the sulfur content of said carbonaceous material.
2. The process of claim 1, wherein said carbonaceous material is a fossil fuel.
3. The process of claim 1, wherein said carbonaceous material is a petroleum product.
4. The process of claim 1, wherein said carbonaceous material is coal.
- 20 5. The process of claim 1, wherein said source of active oxygen is a peroxide.
6. The process of claim 1, wherein said source of active oxygen is aqueous hydrogen peroxide solution.
- 25 7. The process of claim 1, wherein said source of active oxygen is an ozone generator.
8. The process of claim 1, wherein said base is added to said source of active oxygen.
- 30 9. The process of claim 1, wherein said contacting step is carried out by adding a base to said source of active oxygen to form a source of basic active oxygen, then combining said source of basic active oxygen with said carbonaceous material.

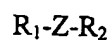
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10. The process of claim 9, where said contacting step is carried out by combining said carbonaceous material, said source of basic active oxygen, and a mutual solvent for said carbonaceous material and said source of basic active oxygen.

5 11. The process of claim 1, where said contacting step is carried out in the presence of a fluid having one of the following structures:



and



15 wherein X and Z are independently selected from C=O and -O-; Y is independently selected from X, -OR₂O- or a direct linkage between R₁ and R₂; R₁ is selected from hydrogen or an independently selected R₂ as defined below; R₂ is selected from straight or branched chain
20 alkyl, alkenyl, or alkynyl having from 1 to 16 carbon atoms, aralkyl having a single ring or multiple ring aryl having from 6 to 24 carbon atoms attached to a straight or branched chain alkyl, alkenyl, or alkynyl as previously defined.

12. The process of claim 11, wherein X and Z are ether linkages.

25 13. The process of claim 1, where said contacting step is carried out in the presence of a fluid selected from the group consisting of: diethyl ether, isopropyl ether, butyl ether, ethyl methyl ether, ethyl n-butyl ether, tetrahydrofuran, dioxane, furan, α-pyran, γ-pyran, s-trioxane, ethylene oxide, propylene oxide, acetone, methyl isobutyl ketone, formaldehyde,
30 acetaldehyde, methanol ethanol, and combinations thereof..

14. The process of claim 1, where said contacting step is carried out in the presence of diethyl ether.

15. The process of claim 1, wherein said base is a hydroxide.
16. The process of claim 1, wherein said base is sodium hydroxide.
17. The process of claim 1, wherein said energy is selected from the group consisting of
5 alpha radiation, beta radiation, gamma radiation, x-radiation, ultraviolet radiation, visible
light radiation, infrared radiation, microwave radiation, radiation resulting from radioactive
decay, ultrasonic energy, and combinations thereof.
18. The process of claim 1, wherein said energy is x-radiation.
- 10 19. The process of claim 1, wherein said energy is ultrasonic energy.
20. The process of claim 1, wherein said source of active oxygen is water-soluble, further
comprising the step of separating said carbonaceous material from said source of active
15 oxygen after said contacting step.
21. The process of claim 1, wherein said contacting step generates a sulfur-containing
gas, further comprising the step of separating said sulfur-containing gas from said
carbonaceous material.
- 20 22. The process of claim 21, further comprising the step of extracting elemental sulfur
from said sulfur-containing gas.
23. The process of claim 21, further comprising the step of oxidizing said sulfur-
25 containing gas, forming sulfur oxides.
24. The process of claim 23, further comprising the step of reacting said sulfur oxides
with lime, forming calcium sulfate.
- 30 25. The process of claim 1, wherein said carbonaceous material as provided is classified
as a high-sulfur fuel, and said carbonaceous material after said contacting step is classified as
a low-sulfur fuel.

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26. The process of claim 1, wherein said carbonaceous material as provided contains at least about 2% by weight elemental sulfur, and said carbonaceous material after said contacting step contains less than about 1% by weight sulfur.

5

27. The process of claim 1, wherein said carbonaceous material as provided contains at least about 2% by weight elemental sulfur, and said carbonaceous material after said contacting step contains less than about 0.5% by weight sulfur.

10 28. The process of claim 1, wherein said carbonaceous material as provided contains at least about 1% by weight elemental sulfur, and said carbonaceous material after said contacting step contains less than about 0.5% by weight sulfur.

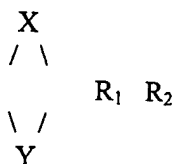
15 29. The process of claim 1, wherein said contacting step is carried out at a temperature between about 32°F (0°C) and about 250°F (121°C).

30. The process of claim 1, wherein said contacting step is carried out at a pressure of from about 0.1 atmosphere to about 2 atmospheres.

20 31. A process for removing sulfur from sulfur-containing carbonaceous materials, comprising:

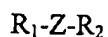
- A. providing a carbonaceous material containing sulfur; and
- B. contacting said carbonaceous material with a source of active oxygen, a base, and a solvent under conditions effective to reduce the sulfur content of said carbonaceous material; said solvent having one of the following structures:

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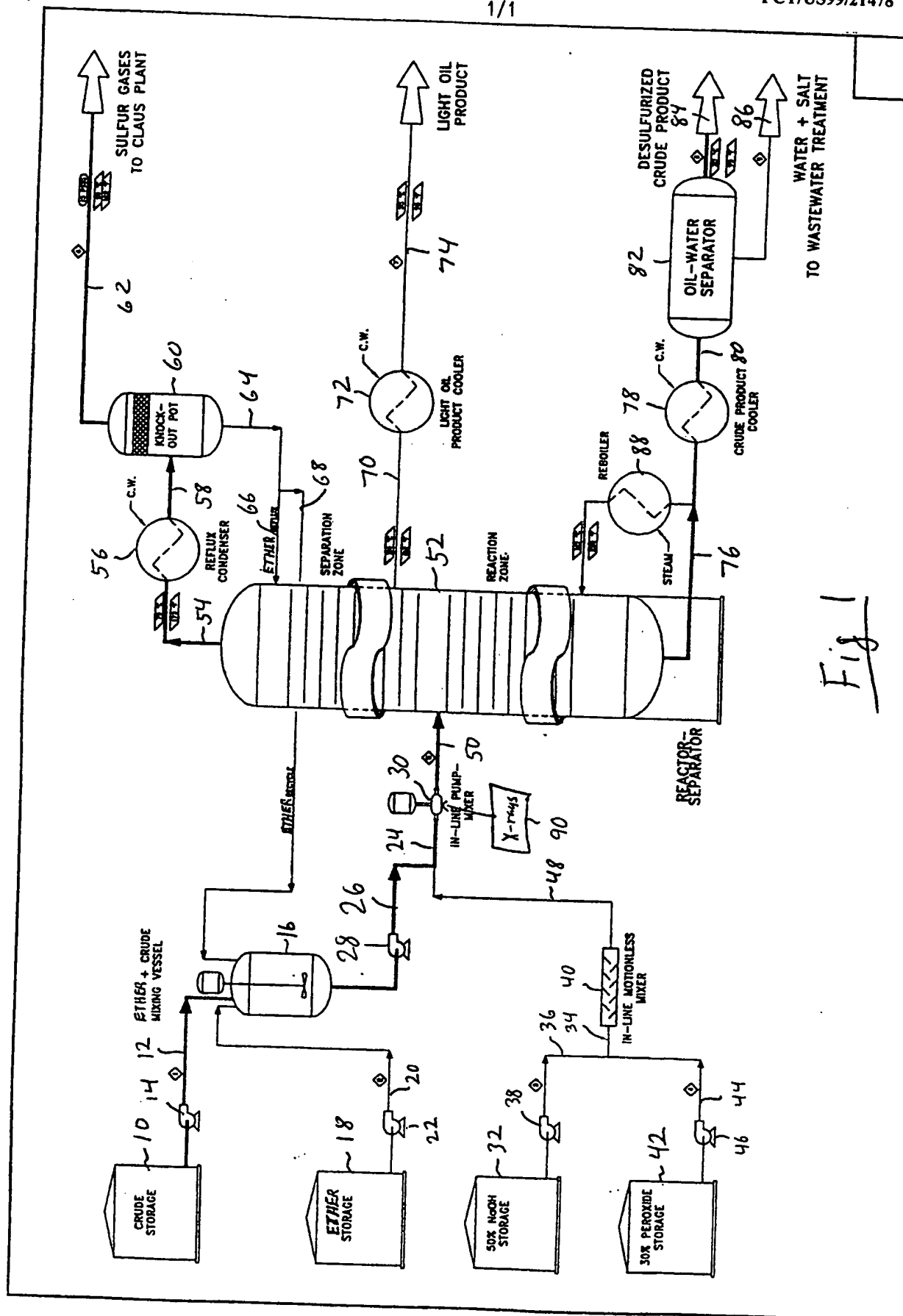
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and



wherein X and Z are each $-O-$; Y is independently selected from $-O-$, $-OR_2O-$, or a direct linkage between R_1 and R_2 ; R_1 is selected from hydrogen or an independently selected R_2 as defined below; R_2 is selected from straight or branched chain alkyl, alkenyl, or alkynyl having from 1 to 16 carbon atoms, aralkyl having a single ring or multiple ring aryl having from 6 to 24 carbon atoms attached to a straight or branched chain alkyl, alkenyl, or alkynyl as previously defined.

- 5
- 10 32. The process of claim 31, wherein said solvent is an aliphatic ether.
33. The process of claim 31, wherein said solvent is diethyl ether.
34. A reduced-sulfur carbonaceous material made by the process of claim 1.
- 15 35. A reduced-sulfur carbonaceous material made by the process of claim 31.
36. Treated California heavy crude oil having a sulfur content of less than about 1% by weight.
- 20 37. Treated California heavy crude oil having a sulfur content of less than about 0.5% by weight.



INTERNATIONAL SEARCH REPORT

Inte. onal Application No

PCT/US 99/21478

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G32/00 C10G27/12 C10G27/14 C10L9/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 391 608 A (DONDELEWSKI MICHAEL A) 5 July 1983 (1983-07-05) column 8, line 37 - line 41; claims 1-7 ---	1-37
Y	US 3 964 994 A (KELLY DECEASED JOE T) 22 June 1976 (1976-06-22) claims 1-4 ---	1-37
A	US 4 152 120 A (BLEILER KENNETH W ET AL) 1 May 1979 (1979-05-01) the whole document ---	1-37
A	US 4 097 244 A (BURK JR EMMETT H ET AL) 27 June 1978 (1978-06-27) the whole document -----	1-37

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

6 January 2000

Date of mailing of the international search report

20/01/2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Application No

PCT/US 99/21478

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